X-Ray and Neutron Diffraction Study of 1,1,1,2,2,2,3,3,3-Nonacarbonyl-1,2;1,3-di-μ-hydrido-μ₃-sulphido-*triangulo*-triosmium

By Brian F. G. Johnson, Jack Lewis,* David Pippard, Paul R. Raithby, and George M. Sheldrick, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Keith D. Rouse, Materials Physics Division, A.E.R.E. Harwell, Didcot, Oxon OX11 0RA

The title complex [Os₃(CO)₉H₂(S)] crystallises in the monoclinic space group $C2/c$ with $a = 20.476(10)$, $b = 13.952(7)$, $c = 12.939(6)$ Å, $\beta = 123.84(3)°$, and $Z = 8$. Simultaneous refinement of a single parameter set to 2 436 X-ray [$(\sin\theta)/\lambda > 0.45$] and 1 292 neutron data has led to R 0.038 (X-ray) and 0.037 (neutron). The two longer edges of the Os₃ isosceles triangle are bridged by hydrides, which lie on the opposite side of the Os₃ plane to the triply bridging sulphur atom. Each osmium is also bonded to three terminal carbonyls. The Os–H–Os linkages can be described as ' open ' three-centre two-electron bent bonds, with little direct Os–Os interaction. Both hydride bridges are significantly asymmetric, the hydrogen atoms being *ca.* 0.025 Å closer to the unique osmium. The mean Os–H distance is 1.819 Å, and both Os–H–Os angles are 106.5(2)°.

X-RAY diffraction studies of heavy-metal carbonyl hydrides provide accurate heavy-atom positions, relatively inaccurate light-atom positions, and very little information about the hydrogen atoms. Neutron diffraction offers a better method of locating the light atoms, but since neutron-beam fluxes are low such studies require large crystals, and much time is required to collect sufficient data for a full anisotropic refinement. In the determination of the crystal and molecular structure of [Os₃(CO)₉H₂(S)] reported here we have tried to optimise the extraction of structural information by fitting a single parameter set to both X-ray and neutron data; full details of the method have been given in the recent study of [Os₃(CO)₁₀(C₂H₃)H].[1] Low-angle X-ray data are excluded from the refinements because they contain information about bonding electrons as well as inner-core electrons (which are assumed to be centred on the nuclear positions); careful treatment of extinction and absorption is also necessary to make the X-ray and neutron data compatible.

The clusters [Os₃(CO)₉H₂(X)] may be obtained by the action of $H_2X = H_2S$, C_6H_6, or C_2H_4 on [Os₃(CO)₁₂], where X is capable of triply bridging the three Os atoms and acting as a four-electron donor to the cluster.[2] This determination of the crystal structure for X = S confirms the structure established in solution by ¹³C n.m.r. spectroscopy.[3] Most neutron-diffraction studies of transition-metal hydrides involve mono- or bi-nuclear species;[4] only three ' edge-bridged ' clusters appear to have been investigated: [Ru₃(CO)₉(CCBuᵗ)H],[5] [Os₃(CO)₁₀(C₂H₃)H],[1] and [Os₃(CO)₁₀H₂].[6]

EXPERIMENTAL

X-Ray Data Collection.—Crystals were deposited from a saturated solution in dichloromethane. Intensities were measured with a Philips PW1100 four-circle diffractometer, graphite-monochromated Mo-K_α radiation, a θ—2θ scan technique, and a single multifaceted crystal of overall dimensions 0.216 × 0.208 × 0.160 mm. Unit-cell dimensions were determined from the angular measurements of 25 strong reflections with $20 < 2\theta < 30°$. Weak reflections which gave $I_t - 2^{\frac{1}{2}}I_t < I_b$ on the first scan were omitted, where I_t is the intensity at the top of the peak and I_b the mean background intensity. Data were collected with a constant scan speed and variable reflection width

(θ range of 0.70 + 0.01 tan θ°) and background measurement time proportional to I_b/I_i, where I_i is the total intensity recorded in the first scan. The 800, 170, and 002 reflections were measured at 6-h intervals throughout the data collection and showed no significant variation in intensity. $\sigma^2(I)$ was calculated as the sum of the variance due to counting statistics and $(0.03I)^2$. Semi-empirical absorption corrections were applied based on a pseudo-ellipsoid model; six parameters were refined to minimise the variation in intensity of nine strong reflections and their symmetry equivalents measured at various azimuthal settings. The value of R for the 418 azimuthal data decreased from 0.087 before correction to 0.034 after; for the full data the transmission factors ranged from 0.026 to 0.004. A total of 3 819 intensities was measured out to $2\theta_{max} = 60°$; equivalent reflections were averaged to give 3 510 unique data with $I > 2.5\sigma(I)$.

Neutron Data Collection.—A large (*ca.* 70 mm³) multi-faceted single crystal was obtained by adding a seed crystal to a warm saturated solution in dichloromethane, which was allowed to cool over 72 h. Neutron intensities were measured on the Andromache Mark VI four-circle diffractometer at A.E.R.E. Harwell with a squashed germanium monochromator and neutron wavelength of 1.181 5(5) Å. The crystal was mounted with the diffractometer ϕ axis collinear with the [110] zone axis. 1 690 Data were collected for $1 < 2\theta < 70°$ using a 60-step ω scan technique and a step width of 0.04°. The $\bar{1}33$ reflection was re-measured every 20 reflections to monitor crystal stability and changes in the neutron flux, but no significant variation in intensity was observed. The data were profile fitted [1] to improve the precision of the weaker reflections. Numerical absorption corrections based on indexed crystal faces were applied (μ 0.08 cm⁻¹); the mean pathlengths derived in this calculation were retained for use in the subsequent extinction corrections. Transmission factors ranged from 0.970 to 0.979. Equivalent reflections were averaged to give 1 292 unique data with $I > 2.5\sigma(I)$.

RESULTS

Crystal Data.—$C_9H_2O_9Os_3S$, $M = 856.7$, Monoclinic, $a = 20.476(10)$, $b = 13.952(7)$, $c = 12.939(6)$ Å, $\beta = 123.84(3)°$, $U = 3 070.2$ Å³, $F(000) = 2 974.83$, $D_e = 3.71$ g cm⁻³, $Z = 8$, Mo-K_α radiation, $\lambda = 0.710 69$ Å, $\mu(\text{Mo-}K_\alpha) = 249.4$ cm⁻¹; neutrons; $\lambda = 1.181 5(5)$ Å, $\mu = 0.08$ cm⁻¹. Space group $C2/c$ from systematic absences and successful structure refinement.

Structure Solution and Refinement.—The structure was

initially solved and refined with the full X-ray data alone. The three Os atoms were found by multisolution Σ_2 sign expansion, and all the non-hydrogen atoms from a subsequent difference synthesis. The structure was refined by blocked-cascade least squares, with anisotropic Os, complex neutral-atom scattering factors, and weights $w = [\sigma^2(F) + 0.001\ 2F_o^2]^{-1}$. An empirical extinction parameter x refined to $0.000\ 18(1)$, where F_c is multiplied by $[1 - (0.000\ 1xF_c^2/\sin\theta)]$. Final residuals were $R = 0.038$ and $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}F_o = 0.043$. A difference electron-density synthesis calculated at this stage showed peaks of height $ca.$ 1.5 e Å^{-3} close to the osmium atoms but did not reveal the positions of the hydrogen atoms.

A difference-Fourier synthesis computed with the neutron data and X-ray thermal and positional parameters revealed two large negative peaks corresponding to the two hydrogen atoms. The structure was refined by full-matrix least squares with all 24 atoms anisotropic. A single set of atomic positional and thermal parameters was fitted simultaneously to the full neutron data and the 2 436 X-ray data with $(\sin\theta)/\lambda > 0.450$ (the low-angle X-ray data would have introduced systematic errors arising from the bonding electron distribution). The final model included X-ray and neutron scale factors and a neutron extinction parameter r^* (defined in ref. 1) which refined to 0.043(1). The weighting scheme was $w = [\sigma^2(F) + gF_o^2]^{-1}$ with g set to 0.001 2 for X-rays and 0.002 0 for neutrons; the mean value of $w\Delta^2$ was relatively independent of the magnitude of F_o or of $\sin\theta$. X-Ray and neutron scattering factors were taken from ref. 7. The final converged residuals were $R = 0.038$ (X-ray), 0.037 (neutron) and $R' = 0.042$ (X-ray), 0.040 (neutron). Table 1 lists the final atomic co-ordinates from the combined refinement. Details of anisotropic

TABLE 1
Atomic co-ordinates ($\times 10^4$)

Atom	x/a	y/b	z/c
Os(1)	3 572(1)	3 409(1)	5 025(1)
Os(2)	4 296(1)	2 248(1)	4 058(1)
Os(3)	3 160(1)	3 770(1)	2 633(1)
S(1)	2 934(1)	2 303(1)	3 326(2)
C(11)	2 654(1)	3 949(1)	4 818(1)
O(11)	2 107(1)	4 288(1)	4 700(2)
C(12)	3 854(1)	2 686(1)	6 492(2)
O(12)	4 036(1)	2 262(2)	7 361(2)
C(13)	4 142(1)	4 570(1)	5 751(1)
O(13)	4 458(1)	5 283(2)	6 124(2)
C(21)	5 389(1)	2 485(1)	4 714(2)
O(21)	6 032(1)	2 602(2)	5 103(2)
C(22)	4 546(1)	1 168(1)	5 143(2)
O(22)	4 697(1)	549(2)	5 805(2)
C(23)	4 147(1)	1 473(1)	2 707(2)
O(23)	4 069(1)	1 032(2)	1 916(2)
C(31)	2 177(1)	4 326(1)	2 099(1)
O(31)	1 577(1)	4 638(2)	1 775(2)
C(32)	2 876(1)	3 605(1)	944(2)
O(32)	2 701(1)	3 566(2)	−57(2)
C(33)	3 665(1)	4 984(1)	2 989(1)
O(33)	3 983(2)	5 706(2)	3 265(2)
H(1)	4 515(2)	3 015(2)	5 336(3)
H(2)	4 132(2)	3 302(2)	3 128(3)

thermal parameters, molecular least-squares planes, and observed and calculated structure factors for both X-ray and neutron data may be found in Supplementary Publication No. SUP 22436 (46 pp.).*

After preliminary X-ray data reduction at the Polytechnic of North London and neutron data reduction at A.E.R.E. Harwell, all calculations were carried out on the

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

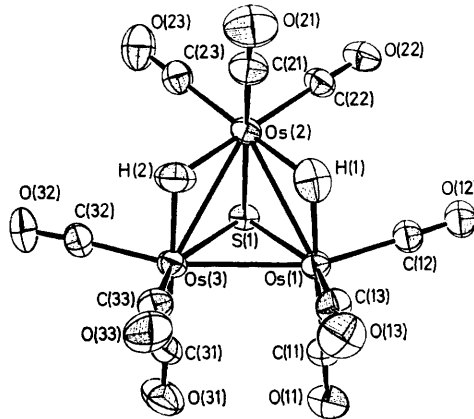Cambridge University I.B.M. 370/165 computer with programs written by G. M. S.

FIGURE 1   ORTEP plot of the molecule, showing 50% probability thermal ellipsoids
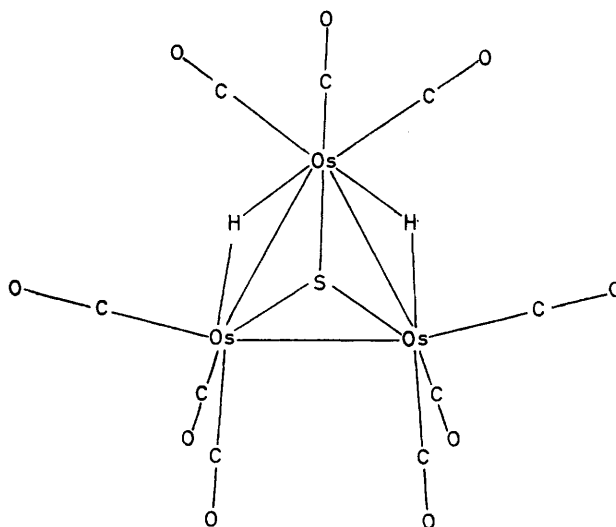

FIGURE 2   Diagramatic representation of the structure

DISCUSSION

The structure consists of discrete $[Os_3(CO)_9H_2(S)]$ molecules; there are no unusually short intermolecular contacts. A single molecule is shown in perspective in Figure 1 and diagrammatically in Figure 2. Interatomic distances and angles are given in Tables 2 and 3. The molecule consists of an isosceles triangle of Os atoms,

TABLE 2
Bond lengths (Å)

Os(1)–Os(2)	2.908(1)	Os(1)–C(11)	1.900(2)
Os(1)–Os(3)	2.764(1)	Os(1)–C(12)	1.932(2)
Os(2)–Os(3)	2.922(1)	Os(1)–C(13)	1.909(2)
Os(1)–S(1)	2.393(2)	Os(2)–C(21)	1.930(2)
Os(2)–S(1)	2.395(2)	Os(2)–C(22)	1.924(2)
Os(3)–S(1)	2.382(2)	Os(2)–C(23)	1.929(2)
Os(1)–H(1)	1.825(3)	Os(3)–C(31)	1.893(2)
Os(2)–H(1)	1.804(3)	Os(3)–C(32)	1.936(2)
Os(2)–H(2)	1.809(3)	Os(3)–C(33)	1.903(2)
Os(3)–H(2)	1.837(3)	C(11)–O(11)	1.145(2)
C(31)–O(31)	1.141(3)	C(12)–O(12)	1.135(3)
C(32)–O(32)	1.136(3)	C(13)–O(13)	1.138(2)
C(33)–O(33)	1.143(2)	C(21)–O(21)	1.128(2)
		C(22)–O(22)	1.131(2)
		C(23)–O(23)	1.127(3)

with the S atom 1.72 Å above the Os_3 plane and approximately equidistant from the three Os atoms. The two longer edges of the triangle are bridged by hydrides, which lie *ca.* 0.86 Å below the metal plane. The angles between the Os(1),S,Os(2) and Os(1),H(1),Os(2) planes, and between the Os(2),S,Os(3) and Os(2),H(2),Os(3) planes, are 169.5 and 164.3° respectively. Each Os is

TABLE 3

Bond angles (°)

Os(2)–Os(1)–Os(3)	62.0(1)	Os(1)–S(1)–Os(2)	74.8(1)
Os(1)–Os(2)–Os(3)	56.6(1)	Os(1)–S(1)–Os(3)	70.8(1)
Os(1)–Os(3)–Os(2)	61.4(1)	Os(2)–S(1)–Os(3)	75.4(1)
Os(2)–Os(1)–S(1)	52.6(1)	C(11)–Os(1)–S(1)	97.8(1)
Os(3)–Os(1)–S(1)	54.4(1)	C(12)–Os(1)–S(1)	106.1(1)
Os(1)–Os(2)–S(1)	52.6(1)	C(13)–Os(1)–S(1)	150.5(1)
Os(3)–Os(2)–S(1)	52.1(1)	C(21)–Os(2)–S(1)	168.1(1)
Os(1)–Os(3)–S(1)	54.8(1)	C(22)–Os(2)–S(1)	95.2(1)
Os(2)–Os(3)–S(1)	52.5(1)	C(23)–Os(2)–S(1)	95.6(1)
Os(2)–Os(1)–C(11)	149.5(1)	C(31)–Os(3)–S(1)	95.7(1)
Os(3)–Os(1)–C(11)	96.3(1)	C(32)–Os(3)–S(1)	108.9(1)
Os(2)–Os(1)–C(12)	100.7(1)	C(33)–Os(3)–S(1)	150.1(1)
Os(3)–Os(1)–C(12)	158.9(1)	Os(1)–Os(2)–C(21)	117.4(1)
Os(2)–Os(1)–C(13)	111.5(1)	Os(3)–Os(2)–C(21)	118.3(1)
Os(3)–Os(1)–C(13)	96.8(1)	Os(1)–Os(2)–C(22)	96.6(1)
C(11)–Os(1)–C(12)	94.4(1)	Os(3)–Os(2)–C(22)	145.5(1)
C(11)–Os(1)–C(13)	91.1(1)	Os(1)–Os(2)–C(23)	147.2(1)
C(12)–Os(1)–C(13)	101.1(1)	Os(3)–Os(2)–C(23)	99.6(1)
Os(2)–Os(1)–H(1)	36.5(1)	C(21)–Os(2)–C(22)	92.3(1)
Os(3)–Os(1)–H(1)	85.8(1)	C(21)–Os(2)–C(23)	93.1(1)
S(1)–Os(1)–H(1)	88.7(1)	C(22)–Os(2)–C(23)	93.8(1)
C(11)–Os(1)–H(1)	173.2(1)	Os(1)–Os(2)–H(1)	37.0(1)
C(12)–Os(1)–H(1)	85.7(1)	Os(3)–Os(2)–H(1)	81.5(1)
C(13)–Os(1)–H(1)	82.3(1)	S(1)–Os(2)–H(1)	89.1(1)
Os(1)–Os(3)–C(31)	94.7(1)	C(21)–Os(2)–H(1)	82.0(1)
Os(2)–Os(3)–C(31)	147.0(1)	C(22)–Os(2)–H(1)	88.0(1)
Os(1)–Os(3)–C(32)	162.7(1)	C(23)–Os(2)–H(1)	174.8(1)
Os(2)–Os(3)–C(32)	105.0(1)	Os(1)–Os(2)–H(2)	83.3(1)
Os(1)–Os(3)–C(32)	96.0(1)	Os(3)–Os(2)–H(2)	37.1(1)
Os(2)–Os(3)–C(33)	111.1(1)	S(1)–Os(2)–H(2)	88.1(1)
C(31)–Os(3)–C(32)	92.7(1)	C(21)–Os(2)–H(2)	83.9(1)
C(31)–Os(3)–C(33)	92.7(1)	C(22)–Os(2)–H(2)	175.7(1)
C(32)–Os(3)–C(33)	99.3(1)	C(23)–Os(2)–H(2)	88.6(1)
Os(1)–Os(3)–H(2)	87.1(1)	H(1)–Os(2)–H(2)	89.3(2)
Os(2)–Os(3)–H(2)	36.4(1)	Os(1)–C(11)–O(11)	178.9(2)
S(1)–Os(3)–H(2)	87.9(1)	Os(1)–C(12)–O(12)	178.6(2)
C(31)–Os(3)–H(2)	176.4(1)	Os(1)–C(13)–O(13)	176.4(2)
C(32)–Os(3)–H(2)	86.5(1)	Os(2)–C(21)–O(21)	178.5(2)
C(33)–Os(3)–H(2)	84.0(1)	Os(2)–C(22)–O(22)	178.2(2)
Os(1)–H(1)–Os(2)	106.5(1)	Os(2)–C(23)–O(23)	178.8(2)
Os(2)–H(2)–Os(3)	106.5(1)	Os(3)–C(31)–O(31)	178.3(2)
		Os(3)–C(32)–O(32)	175.8(2)
		Os(3)–C(33)–O(33)	176.6(2)

also co-ordinated to two equatorial and one axial carbonyls. Although the idealised molecular symmetry is C_s (*m*), with the pseudo-mirror plane passing through Os(2),S,C(21), and O(21), there are some significant distortions; for example, the two chemically equivalent Os–Os bonds differ by 0.014(2) Å. Similar effects have been found in other clusters, *e.g.* a variation of 0.008(1) Å in the Os–Os distances in $[Os_3(CO)_{12}]$,[8] and are sometimes ascribed to 'crystal packing.' There is a close analogy between the structure of $[Os_3(CO)_9H_2(S)]$ and that of the anion $[Os_3(CO)_9H(S)]^-$;[9] in the anion the mean Os–S distance is 2.398(7) Å and there are *two* short Os–Os distances [mean 2.768(1) Å] and *one* long [2.899(1) Å, presumably bridged by the hydride], whereas in $[Os_3(CO)_9H_2(S)]$ the mean Os–S distance is 2.390(4) Å and there are *one* short [2.764(1) Å] and *two* long [mean 2.915(5) Å, hydride-bridged] Os–Os bonds. In general, single hydride bridges lengthen Os–Os bonds relative to

the value in $[Os_3(CO)_{12}]$ [2.877(3) Å],[8] but the triply bridging sulphide shortens all three Os–Os bonds by an amount which is almost as great.

Both Os–H–Os bridges are significantly asymmetric, with the hydrides *ca.* 0.025 Å closer to the unique Os(2); this is presumably a consequence of the different metal-atom environments. A more marked asymmetry was found in the recent combined *X*-ray and neutron study of $[Os_3(CO)_{10}(C_2H_3)H]$,[1] where the 'long' and 'short' Os–H distances are 1.857(4) and 1.813(4) Å, and the Os–H–Os angle of 101.6(2)° is smaller than the value of 106.5(2)° found here for both Os–H–Os bridges. The hydride positions minimise repulsive interactions with the other ligands; H(1) is approximately equidistant from C(12), C(13), C(21), and C(22) (2.56, 2.46, 2.45, and 2.59 Å) whereas H(2) is approximately equidistant from C(21), C(23), C(32), and C(33) (2.50, 2.61, 2.59, and 2.50 Å respectively). The mean S · · · H distance is 2.965 Å and the H(1) · · · H(2) contact is 2.539 Å, 0.14 Å longer than the value in $[Os_3(CO)_{10}H_2]$.[6] Since the H–Os–C angles involving the carbonyl groups *trans* to H are all >173°, the Os–H–Os units are probably best described as 'open'[4] three-centre two-electron bent bonds, with little direct Os–Os bonding. The co-ordination of each Os atom is then distorted octahedral; if the S atom acts as a four-electron donor, two electrons are available to make a single bond between Os(1) and Os(3), resulting in a 48-electron system as in $[Os_3(CO)_{12}]$. The deviations of the Os–C bond lengths from the mean value of 1.93 Å in $[Os_3(CO)_{12}]$[8] are consistent with the assumptions: (*a*) that bonds *trans* to S are shortened by *ca.* 0.025 Å, and bonds *trans* to H by *ca.* 0.032 Å (stronger Os–C π bonding since there is less competition of back donation of *d* electrons from Os); and (*b*) that Os(2)–C bonds are *ca.* 0.028 Å longer than those involving Os(1) or Os(3). Recognition of such trends in other osmium cluster structures is difficult because the C and O (and of course H) positions determined from *X*-ray data alone are much less precise than those found in the combined *X*-ray and neutron study reported here.

REFERENCES

[1] A. G. Orpen, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *Acta Cryst.*, 1978, **B34**, 2466.
[2] A. J. Deeming and M. Underhill, *J. Organometallic Chem.*, 1972, **42**, C60.
[3] A. Forster, B. F. G. Johnson, J. Lewis, and T. W. Matheson, *J. Organometallic Chem.*, 1976, **104**, 225.
[4] R. Bau and T. F. Koetzle, *Pure Appl. Chem.*, 1978, **50**, 55 and refs. therein.
[5] M. Catti, G. Gervasio, and S. A. Mason, *J.C.S. Dalton*, 1977, 2260.
[6] A. G. Orpen, A. V. Rivera, E. G. Bryan, D. Pippard, G. M. Sheldrick, and K. D. Rouse, *J.C.S. Chem. Comm.*, 1978, 723.
[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
[8] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 1977, **16**, 878.
[9] B. F. G. Johnson, J. Lewis, D. Pippard, and P. Raithby, *Acta Cryst.*, 1978, **B34**, 3767.